

Kinetic and isothermal studies of lead ion adsorption onto palygorskite clay

Hao Chen^{a,b}, Aiqin Wang^{a,*}

^a Center of Eco-Material and Green Chemistry, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, People's Republic of China

^b Graduate School of the Chinese Academy of Sciences, Beijing 100049, People's Republic of China

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Abstract

The use of a natural palygorskite clay for the removal of Pb(II) from aqueous solutions for different contact times, pHs of suspension, and amounts and particle sizes of palygorskite clay were investigated. The variations of the pH value of Pb(II) solutions on natural palygorskite in the adsorption process were determined. Batch adsorption kinetic experiments revealed that the adsorption of Pb(II) onto palygorskite clay involved fast and slow processes. It was found that the adsorption mechanisms in the lead/palygorskite system follow pseudo-second-order kinetics with a significant contribution from film diffusion. SEM observations demonstrated that an important interaction at the lead–granule interface occurred during the adsorption process. The adsorption isotherms were described by means of the Langmuir and Freundlich isotherms and the Langmuir model represents the adsorption process better than the Freundlich model. The maximum adsorption capacity of Pb(II) onto natural palygorskite was 104.28 mg g⁻¹.

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1. Introduction

Pb(II) exists intensively in release wastewaters of many industries, such as metal plating, tanneries, oil refining, and mining. It spreads into the environment through soils and water streams and accumulates along the food chain, resulting in a high risk to human health, as lead can affect red blood cells, the nervous system, and the kidneys [1]. As it does not degrade biologically, the control of Pb(II) pollution has special importance for both organisms that live in water and those that benefit from water.

Several treatment processes have been developed over the years to remove heavy metals dissolved in industrial wastewaters: chemical precipitation, ion exchange, and membrane filtration or adsorption [2]. However, most of these techniques have some disadvantages such as complicated treatment process, high cost, and energy use. For adsorption treatment methods, the main disadvantage is the high price of the adsorbents, which

increases the price of wastewater treatment. So, it is necessary to develop some adsorbents with low cost and high efficiency for Pb(II). Clay minerals have great potential as inexpensive and efficient adsorbents due to their large quantities, chemical and mechanical stability, high surface area, and structural properties. In recent years, the great variety of clay minerals as adsorbents has led to much work on their adsorption properties for Pb(II) [3–12].

Palygorskite clay is a silicate clay of which palygorskite is the main component phase. Palygorskite is a crystalline hydrated magnesium silicate with a fibrous morphology, which is composed of talc-like units arranged alternately, generating tunnels of 3.7 × 6.4 Å along the *c*-axis of the fiber [13]. Natural palygorskite particles can adsorb many exchange cations owing to isomorphic substitution during its formation. Its porous structure and adsorbed cations provide it with large specific surface area and moderate cation exchange capacity [14], which is beneficial for the adsorption of heavy metals from solution. Several studies relating to treatment of heavy metal ions, including Pb(II), using palygorskite have been performed [3,8,12]. However, the variation of the pH value of Pb(II) solution in the adsorption process is less reported in this literature.

* Corresponding author.

E-mail address: aqwang@lzb.ac.cn (A. Wang).

Adsorption of metal ions by clay minerals is a complex process involving different mechanisms and is usually described in terms of two basic mechanisms [15,16]: (1) nonspecific adsorption (or cation exchange), which involves rather weak and less selective outer-sphere complexes; (2) specific adsorption, which is based upon adsorption reactions at –OH groups at the mineral surfaces and edges, and which is characterized by more selective and less reversible reactions, including chemisorbed inner-sphere complexes. The variation of the pH of Pb(II) solution is an important parameter in the adsorption process because it can indicate the mechanism of adsorption of Pb(II) onto palygorskite. Therefore, it is necessary to measure the pH so that the adsorption mechanism can be known.

In this study, a natural palygorskite clay from Gansu, China was selected as an adsorbent, and the adsorption capacity of Pb(II) onto the adsorbent was investigated. The effects of parameters such as contact time, pH of suspension solution, and amount and particle size of the adsorbent on adsorption capacity for Pb(II) were studied. To understand the adsorption mechanism, the variation of the pH of the Pb(II) solution in the adsorption process and the different adsorption models that can describe the adsorption of Pb(II) onto natural palygorskite were determined. The adsorption isotherms were described by Langmuir and Freundlich isotherms.

2. Experimental

2.1. Materials and chemicals

The palygorskite clay, gray in color, was obtained from the palygorskite clay mines in Linze of Gansu province, China. The sample was ground and sieved to a given size. Chemical composition of the sample was determined by the PANalytical Company with a Magix PW 2403 XRF Spectrometer and the result was given in Table 1. The cation exchange capacity (CEC) of the sample was determined by the ammonium acetate method [17]. The specific surface area (SSA) of the sample was measured by the glycol dimethyl ether (C₄H₁₀O₂) method [18]. The results obtained were summarized in Table 2. The palygorskite sample was used directly as adsorbent for the adsorption experiments without any pretreatment. The scanning electron microscopy (SEM) analyses were done in a JSM-5600LV with Au sputtering-coated samples fixed in an aluminum stub.

All chemicals were of analytical grade and used as received. A stock solution of Pb(II), prepared by dissolving Pb(CH₃COO)₂·3H₂O in distilled water, was taken as the adsorptive solution. In all experiments distilled water was employed.

2.2. Adsorption studies

Adsorption studies were carried out by mixing known amounts of adsorbent with 40 ml of aqueous solutions of Pb(II). The pH of each suspension was adjusted to a desired value by addition of dilute HCl or NaOH solution (Mettler Toledo 320 pH meter). The mixed solutions were shaken in a thermostatic shaker bath (THZ-98A mechanical shaker) at 120 rpm

Table 1
Chemical composition of palygorskite sample

| Component | Weight (%) |
|--------------------------------|------------|
| SiO ₂ | 57.06 |
| MgO | 8.63 |
| Al ₂ O ₃ | 16.59 |
| Fe ₂ O ₃ | 6.11 |
| CaO | 4.55 |
| TiO ₂ | 0.71 |
| MnO | 0.08 |
| K ₂ O | 3.51 |
| Na ₂ O | 1.35 |
| P ₂ O ₅ | 0.22 |
| SO ₃ | 0.42 |

Table 2
Physicochemical properties of palygorskite sample

| | |
|--|-------|
| Particle size (mesh) | 200 |
| Color | Gray |
| pH | 8.9 |
| Cation exchange capacity (meq/100 g) | 30.0 |
| Special surface area (m ² /g) | 48.66 |

at 30 °C for a given time. After the contact time was completed, the suspension was centrifuged at 5000 rpm for 20 min. Pb(II) remaining in the supernatant was analyzed by EDTA complex titration. The experiments were carried out by varying contact time, pH of suspension, and amount and particle size of adsorbent. The initial concentration of Pb(II) solution was 500 mg L⁻¹ in the above experiments.

Adsorption mechanisms were determined according to the same predefined procedure with Pb(II) concentrations ranging from 25 to 1500 mg L⁻¹. The adsorption capacity of Pb(II) on the adsorbent in the batch test was calculated using the equation

$$q_e = \frac{(C_0 - C_e)V}{m}, \quad (1)$$

where q_e is the equilibrium capacity of lead on the adsorbent (mg g⁻¹), C_0 the initial concentration of lead solution (mg L⁻¹), C_e the equilibrium concentration of lead solution (mg L⁻¹), m the mass of adsorbent used (g), and V the volume of lead solution (L). All assays were carried out in triplicate and only mean values are presented.

3. Results and discussion

3.1. Kinetics studies

Fig. 1 shows the effect of contact time on the adsorption capacity of palygorskite for Pb(II). As can be seen in Fig. 1, q_e increases within 1 h and then it continues to increase at a relatively low speed with contact time until equilibrium is reached at 8 h and remains constant. The result indicates that equilibrium is reached very slowly compared with the facts found by Potgieter et al. [12], who investigated the removal of Pb(II) from aqueous solution on palygorskite and found that the equilibrium time for Pb(II) was only 30 min for concentrations of Pb(II) from 20 to 100 mg L⁻¹. The difference might imply that

Table 3

A comparison of pseudo-first-order, pseudo-second-order, and intraparticle diffusion kinetic model rate constants calculated from experimental data

| Adsorbent | Pseudo-first-order | | | Pseudo-second-order | | | Intraparticle diffusion | | |
|--------------|---------------------------------|------------------------------|-------|---------------------------------|---|-------|---|-------------------------------|-------|
| | q_e (mg g^{-1}) | k_1 (h^{-1}) | r^2 | q_e (mg g^{-1}) | k_2 ($\text{g mg}^{-1} \text{h}^{-1}$) | r^2 | k_i ($\text{mg g}^{-1} \text{h}^{-1/2}$) | C (mg g^{-1}) | r^2 |
| Palygorskite | 45.27 | 0.3076 | 0.956 | 62.70 | 0.0292 | 0.999 | 16.80 | 19.63 | 0.984 |

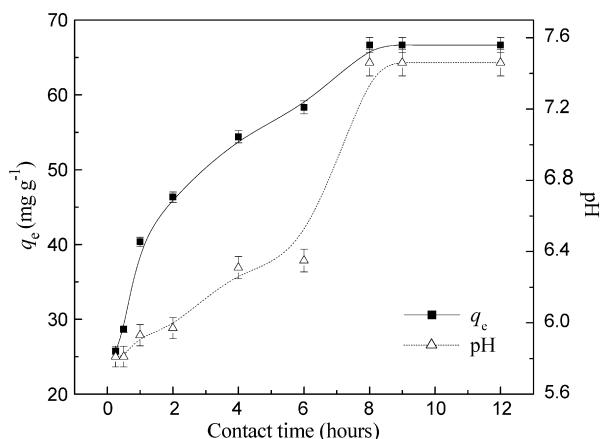


Fig. 1. Effect of contact time on the adsorption capacity of palygorskite for Pb(II) (amount of palygorskite 0.30 g, 200 mesh, pH of suspension 6.0).

the adsorption sites on the palygorskite clay are not well exposed and there are more complex adsorption mechanisms in this study.

In order to investigate the adsorption kinetics of Pb(II) on palygorskite, three different kinetic models, pseudo-first order, pseudo-second order, and intraparticle diffusion, have been used to fit experimental data obtained from batch Pb(II) removal experiments. The pseudo-first-order kinetic model has been widely used to predict metal adsorption kinetics. It was suggested by Lagergren [19] for the adsorption of solid/liquid systems and its formula is given as

$$\frac{dq_e}{dt} = k_1(q_e - q_t). \quad (2)$$

After integration with the initial condition $q_t = 0$ at $t = 0$, the following equation can be obtained,

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}, \quad (3)$$

where q_t is the adsorption capacity at time t (mg g^{-1}) and k_1 (h^{-1}) is the rate constant of the pseudo-first-order adsorption.

The kinetic data were further analyzed using Ho and McKay's pseudo-second-order kinetic model, expressed as [20]

$$\frac{dq_e}{dt} = k_2(q_e - q_t)^2. \quad (4)$$

When the initial condition is $q_t = 0$ at $t = 0$, integration leads to the equation

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}, \quad (5)$$

where k_2 ($\text{g mg}^{-1} \text{h}^{-1}$) is the rate constant of the pseudo-second-order adsorption.

The kinetic data can also be analyzed by an intraparticle diffusion kinetics model, formulated as [21]

$$q_t = k_i t^{1/2} + C, \quad (6)$$

where k_i ($\text{mg g}^{-1} \text{h}^{-1/2}$) is the intraparticle diffusion rate constant and C (mg g^{-1}) is a constant.

By testing the three plots of $\log(q_e - q_t)$ versus t , (t/q_t) versus t , and q_t versus $t^{1/2}$, the rate constants k_1 , k_2 , and k_i and correlation coefficients can be calculated and the results are shown in Table 3. As seen from Table 3, compared to the pseudo-first-order and intraparticle diffusion kinetics models, a good correlation coefficient (r^2) was obtained for the pseudo-second-order kinetic model, which indicates that Pb(II) adsorption onto palygorskite follows the pseudo-second-order rate expression. The fact that the second-order kinetics is the best fit model for the adsorption of Pb(II) onto palygorskite indicates that the adsorption rate of Pb(II) depends on the concentration of ions at the adsorbent surface and the behavior over a whole range of adsorption is in agreement with chemical adsorption being the rate-controlling step [22,23]. In addition, it is necessary to note that the intercept (C) as proposed by Eq. (6) was not zero but a large value (19.63 mg g^{-1}), indicating that intraparticle diffusion may not be the controlling factor in determining the kinetics of the process [24].

It is interesting to note that Pb(II) on palygorskite attains equilibrium after a long time under the experimental conditions studied (Fig. 1). The whole adsorption process involves fast and slow adsorption stages (respectively, 0–1 and 1–8 h). This result may indicate that film diffusion and intraparticle diffusion together controlled the whole adsorption process [25]. To determine the actual process involved in the present adsorption, of the following equation can be employed for the adsorption dynamics,

$$F = 1 - \frac{6}{\pi^2} \sum_1^{\infty} \left(\frac{1}{n^2} \right) \exp(-n^2 B_t), \quad (7)$$

where F is the fractional attainment of equilibrium at time t and is obtained by using

$$F = Q_t / Q_{\infty}, \quad (8)$$

where Q_t and Q_{∞} are amounts adsorbed after time t and after infinite time, respectively; n is the Freundlich constant of the adsorbate; and B_t is a calculated mathematical function of F (and vice versa) derived from Reichenberg's table [26].

Rearranging the above equation gives

$$B_t = -\ln(1 - F) - 0.4799, \quad (9)$$

$$B_t = 6.28318 - 3.2899F - 6.28318(1 - 1.0470F)^{1/2}. \quad (10)$$

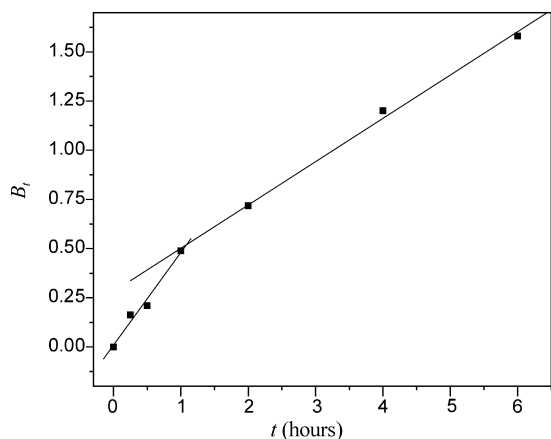
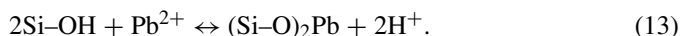
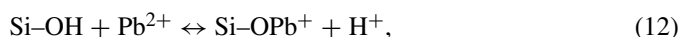
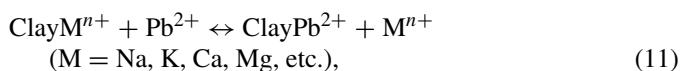


Fig. 2. B_t vs t plot for Pb(II) adsorption onto palygorskite.

Equation (10) was used for values of F from 0 to 0.85 and Eq. (9) for values from 0.86 to 1. Thus the value of B_t can be calculated for each value of F using Eqs. (9) or (10). The B_t values were plotted against t as shown in Fig. 2. The linearity of this plot can be used to distinguish between film diffusion and intraparticle diffusion mechanisms. If this plot is a straight line passing through the origin, adsorption will be governed by a particle-diffusion mechanism, otherwise by film diffusion [27]. It is obvious from Fig. 2 that the nature of the graph is not a straight line, indicating that the film diffusion mechanism is the rate-controlling step in the whole adsorption process. In fact, the obtained graph can be plotted into two portions: 0–1 and 1–6 h. Although the two plots do not both pass through the origin, the calculated regression coefficient for the second portion is higher than that for the first portion (respectively, 0.999 and 0.989), which indicates that the intraparticle diffusion mechanism should become more significant when the adsorption time becomes longer (>1 h).

The above result reveals that Pb(II) adsorption onto palygorskite undergoes two stages—fast and slow adsorption processes. In the case of the fibrous clay minerals, retention of heavy metal on them can be through adsorption and/or cation exchange reactions [14]. And adsorption can be considered as taking place mainly on the silanol groups (Si–OH) of palygorskite [3,8]. Hence, the variation of pH of the final solutions with increasing time was measured to know the adsorption mechanism and the result is shown in Fig. 1. It is known that the initial adsorption stage is mainly controlled by film diffusion (external mass transfer); the principal mechanism of interaction should be cation exchange, which can be represented by Eq. (3). Consequently, the pH of the final solution increases generally with increasing contact time due to the lower hydrolyzed constant of Pb(II) compared to M^{n+} on palygorskite:



The second stage is a gradual adsorption stage where film diffusion and intraparticle diffusion are operating simultaneously.

Diffusion to internal site and adsorption to available adsorption sites, i.e., mainly specific adsorption of surface sites (Si–OH) on palygorskite clay by Eqs. (12) and/or (13) and cation-exchange reaction by Eq. (11), both occur. The pH of the final solution continues to increase with the increase of contact time from 1 to 4 h and then decreases at 6 h, which implies that the adsorption mechanism should become more significant when adsorption time exceeds 4 h.

In this study, SEM is used to probe the change in morphological features of natural palygorskite and Pb-adsorbed palygorskites (Fig. 3). It is clearly observed in Fig. 3 that the surface morphology of Pb-adsorbed palygorskite is different from that of natural palygorskite. The natural palygorskite clay shows loose aggregates with porous structure. After adsorption, large amounts of pores on clay disappear with an increase in adsorption time and as the adsorption time reaches 1 h, the surface of the clay demonstrates compact aggregates and does not change visibly with further adsorption. SEM results show that the surface morphology of the palygorskite clay changed evidently during the adsorption process, indicating that an important interaction at the lead-granule interface occurred in the experimental conditions.

Since palygorskite clay is a mixture of several minerals containing several different types of adsorption sites, it is most likely that multiple slow reaction mechanisms were responsible for the slow-phase Pb(II) adsorption onto palygorskite clay. Similar time-dependent metal adsorption behavior is reported by other researchers [25]. It is confirmed by the variation of pH vs time that it takes a determinate time to reach complete equilibrium for some interactions, such as the interface of palygorskite and water, the interface complexation, and interface ion exchange during adsorption. To improve the adsorption capacity and prevent precipitation of Pb(II), 6 h was selected as the contact time for the rest of the batch experiments.

3.2. Effect of amount of palygorskite

Amount of adsorbent is an important parameter because this factor determines the adsorption capacity of an adsorbent for a given initial concentration of the adsorbate. Effect of the amount of palygorskite on the q_e and pH of the final solution is shown in Fig. 4. Clearly, q_e decreases with increasing amount of palygorskite. This result shows that the amount of Pb(II) adsorbed per unit weight of palygorskite, i.e., the adsorption efficiency of palygorskite, decreases with increasing amount of palygorskite. Naseem and Tahir [7] and Potgieter et al. [12] reported similar findings for Pb(II) adsorption from aqueous solutions onto bentonite and palygorskite, respectively.

As can be seen in Fig. 4, the pH of the final solution increases gradually with increase in the amount of palygorskite. This may be explained by the following fact. The surface of natural palygorskite is negative owing to isomorphous substitution during its form process: negatively charged sites on the surface of palygorskite particles will increase with an increase of palygorskite mass, which can induce more H^+ ions to adsorb onto palygorskite surface and result in an increase in the pH of the final solution. In addition, carbonate minerals contained in pa-

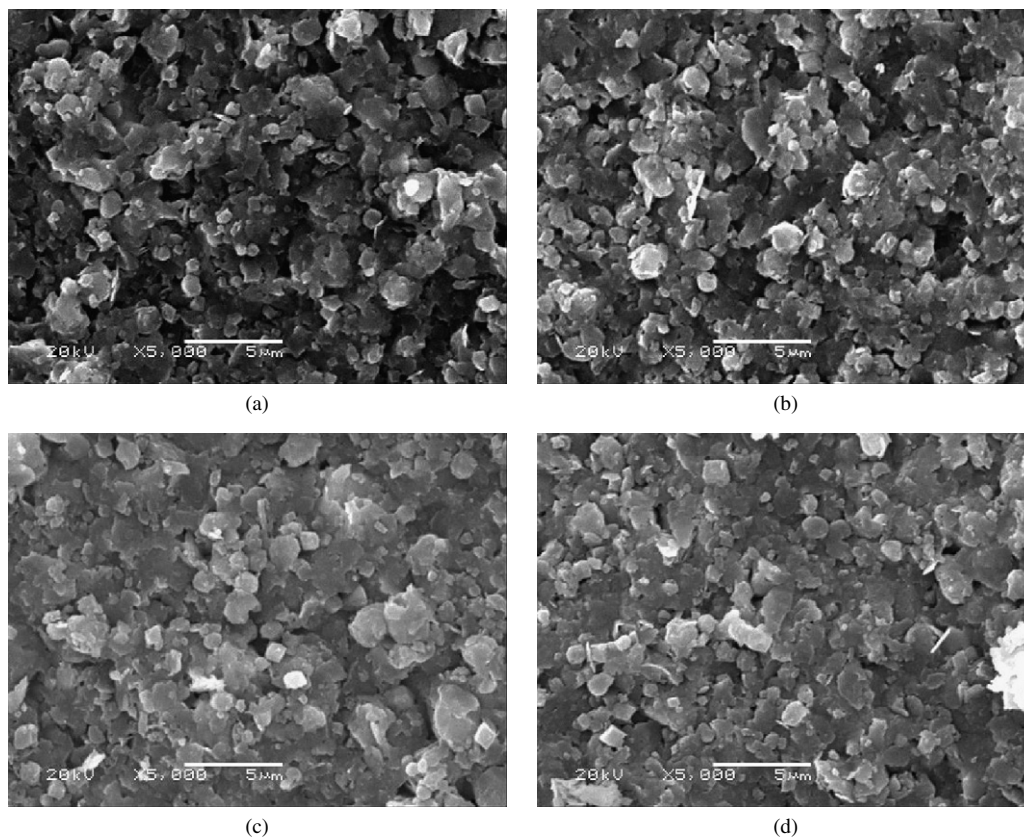


Fig. 3. SEM micrographs of (a) natural palygorskite and Pb-adsorbed palygorskites after (b) 0.5 h, (c) 1 h, and (d) 4 h.

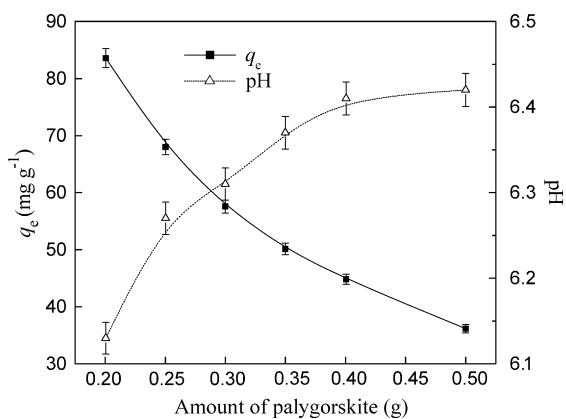


Fig. 4. Effect of amount of palygorskite on Pb(II) adsorption (200 mesh, pH of suspension 6.0, contact time 6 h).

lygorskite clay are also the reason for an increase in the pH of the solution. Considering the cost and efficiency of wastewater treatment, an amount of 0.30 g may be a good selection for the added mass of palygorskite for the rest of the batch experiments.

3.3. Effect of particle size of palygorskite

Fig. 5 shows that q_e increases gradually with increasing mesh, i.e., decreasing particle size of palygorskite. This is an expected result because as the particle size of palygorskite decreases, the number of activated adsorption sites on the surface of palygorskite particles increases and these particles attach

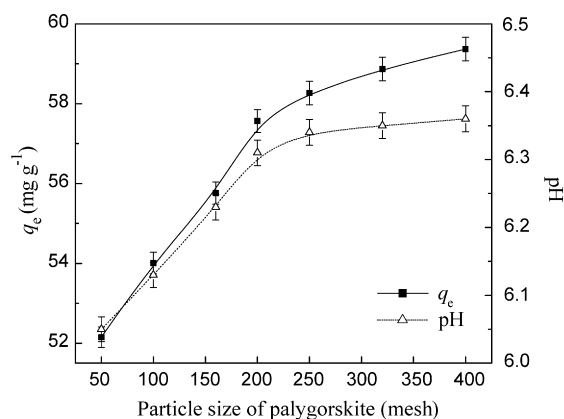


Fig. 5. Effect of particle size of palygorskite on Pb(II) adsorption (amount of palygorskite 0.30 g, pH of suspension 6.0, contact time 6 h).

more Pb(II) to their surfaces. When the particle size of palygorskite becomes smaller (>200 mesh), q_e shows a relative slow increase, which indicates that q_e is rarely affected by the particle size of palygorskite in the above conditions. Similar results were reported by Álvarez-Ayuso and García-Sánchez [8] and Bektas et al. [9], who used palygorskite and sepiolite as adsorbents for Pb(II), respectively. Variation of the pH of the final solution with increasing mesh of palygorskite is consistent with that of q_e . The reason for this result is similar to that in the above discussion for the effect of amount of palygorskite on pH. Considering the problems in actual application, such as energy use and the separation of solid and liquid, 200 mesh is an appropriate choice.

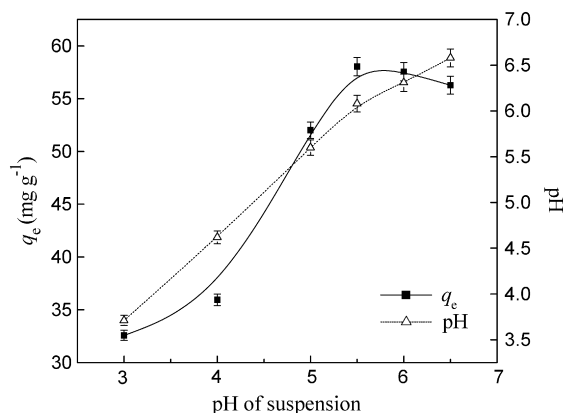


Fig. 6. Effect of pH of suspension on adsorption of palygorskite for Pb(II) (200 mesh, amount of palygorskite 0.30 g, contact time 6 h).

3.4. Effect of pH of suspension

The pH of a suspension is an important factor that can affect the form and the quantity of Pb(II) in water, the form and quantity of a mineral's surface sites, and the interaction of the mineral and Pb(II). The pH of the final Pb(II) solution is especially indicative of the properties of the liquid system because it is the result of interaction between the mineral and the Pb(II) solution. So the influence of the pH of the initial suspension on the adsorption of Pb(II) onto palygorskite was examined in the pH range of 3 to 6.5 (Fig. 6). It can be seen from the graph that q_e increases with an increase in the pH of the solution to a maximum around a pH value of 5.5, and then decreases as pH is close to neutral. When pH value is low (<4), a high concentration of H⁺ ions compete with Pb(II), resulting in the suppression of Pb(II) adsorption on the palygorskite surface. Consequently, a low q_e of Pb(II) occurs on palygorskite. As pH increases to 5.0, it can be deduced according to the isoelectric point (iep) of palygorskite at about 4.0–4.5 [28] that the palygorskite surface becomes negatively charged as a whole and more Pb(II) can be adsorbed onto it, so that the q_e of Pb(II) increases perceptibly. This trend of increase continues until pH reaches 5.5. The decreased q_e of Pb(II) at higher pH values may be due to the following process. High pH conditions reduce the mobility of Pb(II) due to the decrease in the exchangeable form, i.e., Pb(II), resulting in a decrease in the contact probability between adsorbent and adsorbate. This trend of q_e vs pH of the initial suspension is consistent with the removal of Pb(II) by volcanic ash soil [29], kaolinitic clay [4], and palygorskite [12], though these authors studied the pH of the initial Pb(II) solution.

On the base of the above tests on the factors, experimental adsorption conditions were determined that included particle size: 200 mesh; amount of palygorskite: 0.30 g; pH of initial suspension: 6.0; and contact time: 6 h.

3.5. Adsorption isotherms

To identify the mechanism of the adsorption process, the adsorption of Pb(II) onto palygorskite is determined as a function of equilibrium (residual) Pb(II) concentration (C_e) and the cor-

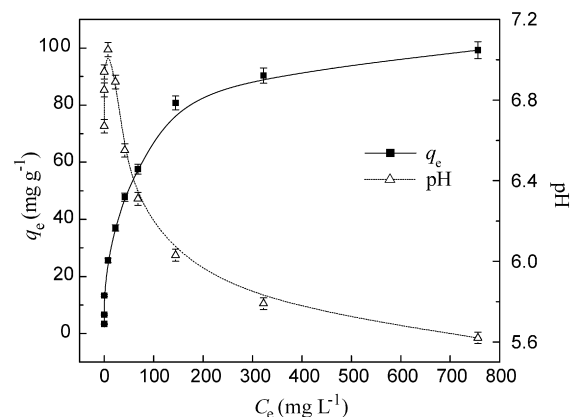


Fig. 7. Adsorption isotherm of Pb(II) on palygorskite (200 mesh, amount of palygorskite 0.30 g, pH of suspension 6.0, contact time 6 h).

responding adsorption isotherms are plotted in Fig. 7. At low concentrations of Pb(II) solutions, the pH of the final solution increased with increased initial concentration of the Pb(II) solution, which indicated that cation exchange was a dominant mechanism under these adsorption conditions. However, surface complexation should be the dominant mechanism at higher concentrations of Pb(II) solutions, which was confirmed by an evident decrease in the pH of the final solution. According to the classification of Giles et al. [30], the isotherm seems to be of the L type, indicating that the Pb(II) has a high affinity for the palygorskite surface.

The data can then be correlated with a suitable isotherm. The adsorption process is normally described by the Langmuir [31] and the Freundlich [32] isotherms. The Langmuir adsorption isotherm assumes that adsorption occurs at specific homogeneous sites within the adsorbent and has found successful application in many studies of monolayer adsorption. The linear form of the Langmuir isotherm equation is written as

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m}, \quad (14)$$

where q_e is the equilibrium capacity of lead on adsorbent (mg g⁻¹), C_e is the equilibrium concentration of lead solution (mg L⁻¹), q_m is the monolayer adsorption capacity of the adsorbent (mg g⁻¹), and b is the Langmuir adsorption constant (L mg⁻¹) and is related to the free energy of adsorption.

The Freundlich model assumes a heterogeneous adsorption surface with sites that have different energies of adsorption and are not equally available. The Freundlich isotherm is more widely used but provides no information on the monolayer adsorption capacity, in contrast to the Langmuir model. Its linearized form can be written as

$$\log q_e = \log K_f + \frac{1}{n} \log C_e, \quad (15)$$

where K_f (L g⁻¹) and n (dimensionless) are the Freundlich adsorption isotherm constants, being indicative of the extent of adsorption and the degree of nonlinearity between solution concentration and adsorption, respectively.

Adsorption equations were obtained from experimental data with Eqs. (14) and (15). The isotherm constants and correlation coefficients were calculated from the linear Langmuir and

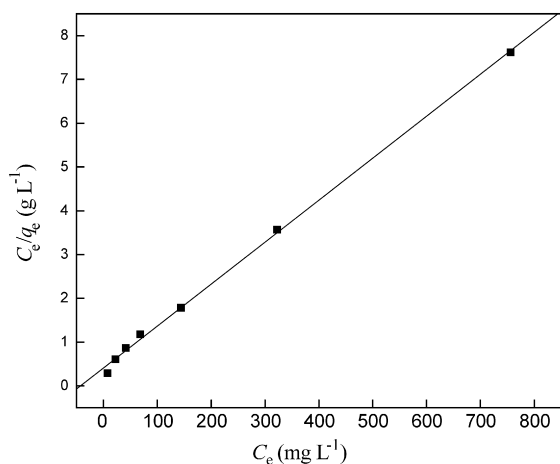


Fig. 8. Langmuir plot for the adsorption of Pb(II) onto palygorskite.

Table 4

Langmuir and Freundlich constants and correlation coefficients associated with adsorption isotherms of Pb(II) onto palygorskite

| Adsorbent | Langmuir equation | | | Freundlich equation | | |
|--------------|-----------------------------|---------------------------|-------|---------------------|------|-------|
| | q_m (mg g ⁻¹) | b (L mg ⁻¹) | r^2 | K_f | n | r^2 |
| Palygorskite | 104.28 | 0.0235 | 0.999 | 14.72 | 3.23 | 0.980 |

Table 5

A comparison of maximum adsorption capacities of Pb(II) on different clays

| Clays | q_m (mg g ⁻¹) | References |
|-----------------|-----------------------------|------------|
| Kaolinite | 11.52 | [10] |
| Montmorillonite | 31.05 | [10] |
| Sepiolite | 35.19 | [5] |
| Palygorskite | 37.2 | [8] |
| Palygorskite | 62.11 | [12] |
| Palygorskite | 104.28 | This study |

Freundlich plots by plotting C_e/q_e vs C_e (Fig. 8) and $\log q_e$ vs $\log C_e$ (Fig. 9) and are represented in Table 4. The Langmuir equation represent the adsorption process very well; the r^2 value is higher for the Langmuir isotherm than for the Freundlich isotherm. This may be due to homogeneous distribution of active sites on the palygorskite surface [9]. It is also reported in some studies that the adsorption of Pb(II) onto palygorskite is described well by the Langmuir equation [8,12].

The K_f value of the Freundlich equation (Table 4) indicates that palygorskite has a very high adsorption capacity for lead ions in aqueous solutions. n values between 1 and 10 indicate beneficial adsorption [33]. The value of maximum adsorption capacity (q_m) calculated from the Langmuir isotherm in this study is much higher than that of those reported in the literature (Table 5). In terms of the same clay, i.e., palygorskite, the q_m of the mineral used in this study is also maximal. This result indicates that the studied palygorskite possesses a very high adsorption capacity, so that the mineral is very useful in removing Pb(II) from aqueous solutions.

4. Conclusions

The removal of Pb(II) with palygorskite clay obtained from Gansu province of China was systematically investigated un-

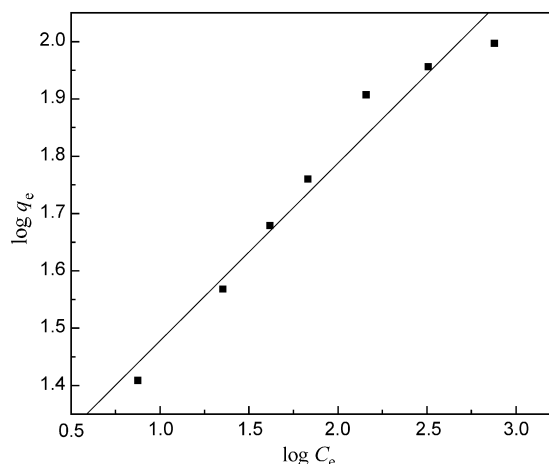


Fig. 9. Freundlich plot for the adsorption of Pb(II) onto palygorskite.

der various conditions. The adsorption capacity of Pb(II) on palygorskite increased with the increase of contact time, mesh of adsorbent, and pH of suspension, but with the decrease of amount of adsorbent. A batch adsorption kinetic experiment revealed that Pb(II) adsorption onto palygorskite clay was well represented by the pseudo-second-order kinetic model. It can be concluded that film diffusion and intraparticle diffusion are simultaneously operating in the whole adsorption process. SEM observations indicated that an important interaction at the lead-granule interface occurred during the adsorption process. The Langmuir model represented the adsorption process better than the Freundlich model for the adsorbent and the maximum adsorption capacities of Pb(II) onto natural palygorskite were 104.28 mg g⁻¹. The results of the present study show that Pb(II) can be adsorbed successfully in significant amounts on palygorskite, indicating that natural palygorskite clay from Gansu province of China is a good adsorbent for the removal of Pb(II) from aqueous solution.

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